

1.

**Professor Robert H. Grubbs
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125
(818) 395-6003 FAX: 818564 9297
rhg@starbase1.caltech.edu**

**Air Force Office of Scientific Research
F49620-92-J-0295
Conjugated Polymers From Cyclohexadienediol Monomers**

**Progress Report
September 1, 1995**

| DTIC QUALITY INSPECTED 3

19970613 049

20 MAR 1996

REPORT DOCUMENTATION PAGE

AFOSR-TR-97

0254
581 data sources,
aspect of this
1215 Jefferson

Public reporting burden for this collection of information is estimated to average 1 hour per response. Gathering and maintaining the data needed, and completing and reviewing the collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	July 31, 1996	Final Technical 6/1/95-5/31/96

4. TITLE AND SUBTITLE	Living Catalysts for Cyclohexadiene Polymerization
-----------------------	--

6. AUTHOR(S)

Robert H. Grubbs

5. FUNDING NUMBERS

F49620-92-J-0295

3484/S2

G105D

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
--	--

California Institute of Technology Mail Stop 213-6 Pasadena, CA 91125	
---	--

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
---	--

AFOSR/NL 11 Duncan Avenue, Suite B115 Bolling AFB DC 20332-0001	F49620-92-J-0483
---	------------------

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
--	------------------------

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.	
---	--

13. ABSTRACT (Maximum 200 words)

ROMP polymerization has become an important method for the preparation of polyphenylenevinylenes and polynaphthylenevinylene. The new route allows the band gap and processing properties of the polymers to be varied by the use of side chains and functional groups. These materials are being used to fabricate electroluminescent devices with tunable colors. New techniques have been developed for the synthesis of the starting barrelenes and benzobarrelenes. These synthesis start from the ICI diol system that was used in the preparation of polyparaphenylene. A key to these developments is the availability of well defined catalysts, considerable effort has been devoted to the design and synthesis of new complexes that will catalyze the ROMP polymerization reaction and to develop new procedures which will control the molecular weight and livingness of those systems known. The students involved in this work have gained experience in polymer synthesis, catalyst development and the fabrication of devices.

14. SUBJECT TERMS	15. NUMBER OF PAGES
-------------------	---------------------

	2
--	---

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
---------------------------------------	--	---	----------------------------

UNCLASSIFIED

UNCLASSIFIED

UNCLASSIFIED

unlimited

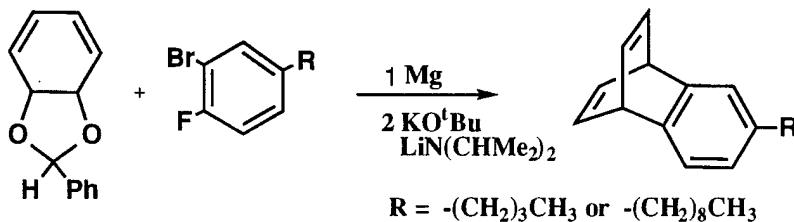
NSN 7540-01-280-5500

2. Objectives: no change

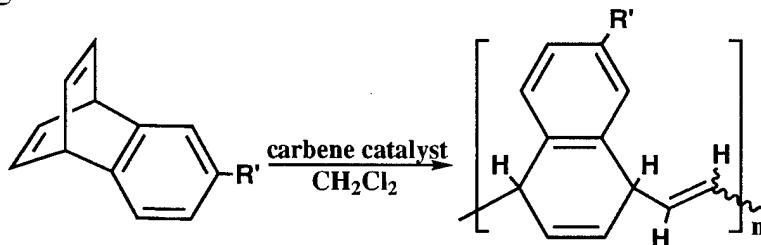
3. & 4. Progress and Technical Accomplishments

Polyarylenevinylene

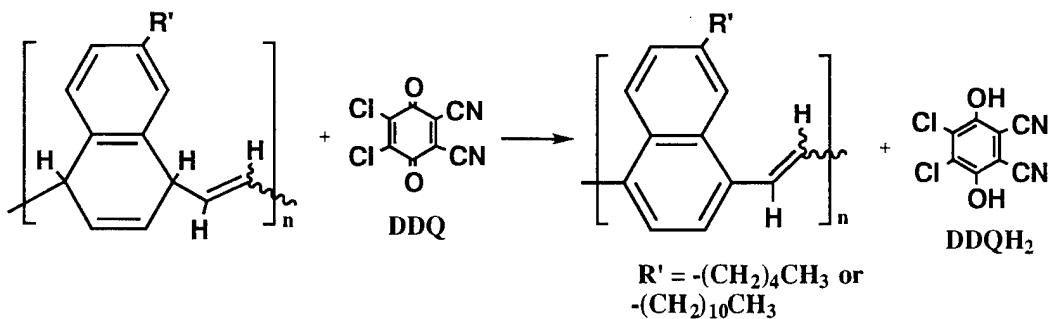
The ICI cyclohexadiene monomer has been used to prepare poly(arylenevinylene) derivatives through a precursor route. The polyarylene vinylenes show interesting properties and some derivatives have been used to fabricate photoemitting diodes. A general route to polynaphthalene vinylenes has been developed that is now being expanded in to the synthesis of block polymers. A simple route to substituted benzynes precursors (**8a,b**) was developed and the resulting benzenes were added to the ICI monomer. The adducts could be converted to benzobarrelene analogs by the treatment of the benzaldehyde acetal derivative with a strong base such as LDA.



The resulting benzobarrelenes could be polymerized to in high yields with a variety of ROMP catalysts. These living systems could be used to control the molecular weight and molecular weight distribution.



The resulting soluble polymers could then be converted to the soluble vinylenenaphthylene with a variety of oxidizing agents, however DDQ was the most effective.



The UV/Vis spectrum of the fully conjugated derivatives displays a strong absorbance at 448- 450 nm, which demonstrates the formation of an extended p-conjugation in the oxidized polymer after the dehydrogenation. When excited at 440 nm, the fluorescence emission spectra of the conjugated polymers show strong signals at 583 nm and 572 nm respectively. By visual observation, solutions of the conjugated polymers glow yellow orange under UV irradiation. In preliminary studies, electroluminescence devices have been fabricated by spin coating using these materials. A key finding was that good internal electroluminescence quantum efficiencies of up to 0.05% could be obtained using an air stable Aluminum electrode.

Derivatives that contain halogens as electron withdrawing groups have been prepared and converted to polymers. It has been found that these derivatives can be used to tune the emission spectrum of the resulting polymer for example a polymer with red fluorescence has been reported. With support from another agency, this work has continued as a method for the preparation of a variety of block polymers and related systems. A number of new methods of controlling the polymerizations were uncovered during this work and is now being studied in detail in a mechanistic study supported by the NSF.

Since the monomers that are being prepared are new substrates for ROMP, a method of predicting which compounds will polymerize has been developed and is being applied to a number of new substrates.

Polyparaphenylenes: The final papers on the synthesis of polyparaphenylenes have been published. A collaboration with A. MacDiarmid at U. of Penn has resulted in the conversion of the precursors into extremely stable films of PPP. Samples of the high molecular weight, linear precursor to polyparaphenylenes that was prepared were sent to the University of Dayton, Edwards Airforce Base and to other federal laboratories. Other applications in the construction of blue electroluminescence diodes and in the development of a high density battery are being explored.

5. Graduate students supported during this effort:

Michael Wagaman

Thomas Wilhelm

6. Publications:

"Transition Metal Catalyzed Polymerizations of Heteroatom-Submitted Cyclohexadienes: Precursors to Poly(paraphenylenes)." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *Polymer Preprints* **1991**, 32, 236-237.

"Transition-Metal-Catalyzed Polymerization of Heteroatom-Functionalized Cyclohexadienes: Stereoregular Precursors to Poly(*para*-phenylene)." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* **1992**, 114, 3167-3169.

"Ring-Opening Metathesis Polymerization of Substituted Bicyclo[2.2.2]-octadienes: A New Precursor Route to Poly(1,4-Phenylene-Vinylene)." V. P. Conticello, D. L. Gin, and R. H. Grubbs, *J. Am. Chem. Soc.* **1992**, 114, 9708-9710

"Highly Unsaturated Oligomeric Hydrocarbons: a-(Phenylethynyl)-w-phenylpoly[1,2-phenylene(2,1-ethynediyl)]." R. H. Grubbs and D. Kratz, *Chem. Ber.* **1993**, 126, 149-157.

"Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 1. Precursor Design and Synthesis." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* **1994**, 116, 10507-10519

"Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 2. The Effects of Polymer Stereochemistry and Acid Catalysts on Precursor Aromatization." D. L. Gin, V. P. Conticello, and R. H. Grubbs, *J. Am. Chem. Soc.* **1994**, 116, 10934-10947.

"New Syntheses of Benzobarrelenes." L. Pu and R. H. Grubbs, *J. Org. Chem.* **1994**, 59, 1351-1353.

"Routes to Conjugated Polymers with Ferrocenes in their Backbones: Synthesis and Characterization of Poly(ferrocenylene divinylene) and Poly(ferrocenylene butenylene)." C. E. Stanton, T. R. Lee, R. H. Grubbs, N. S. Lewis, J. K. Pudelski, M. R. Callstrom, M. S. Erickson, M. L. McLaughlin, *Macromolecules* **1995**, 28, 8713-8721.

"Red-Orange Electroluminescence with New Soluble and Air-Stable Poly(Naphthalene-Vinylene)s." S. Tasch, W. Graupner, W. Leising, G. Pu, M. W. Wagaman, and R. H. Grubbs, *Advan. Mater.* **1995**, 7(11), 903.

"Synthesis of Poly-(1,4-Naphthalene Vinylenes): Metathesis Polymerization of Benzobarrelenes." L. Pu, M. W. Wagaman, and R. H. Grubbs, *Macromolecules* **1996**, 29, 1138-1143.

Chapters

"Ring -Chain Equilibria in Ring-Opening Metathesis Polymerization (ROMP) of Cycloolefins" Zhongren Chen, J. A. Kornfield, J.P. Claverie, R.H. Grubbs, *Polymer Preprints*, **1994**, 692.

7. Interactions/Transitions:

(a) Participation at meetings, conference, seminars, etc.:

209th ACS National Meeting, Anaheim, CA
April 2-6, 1995

210th ACS National Meeting, Chicago, IL
August 20-24, 1995

(b) Consultative and advisory functions to other laboratories and agencies. (Provide subject matter, institutions, locations, dates, and names of individuals involved.)

NRC Polymers, Macromolecules Advisory Board,
Material to G. Leissing for fabrication of LED

(c) Transitions.

8. New discoveries, inventions, or patent disclosures. none

9. Honors/Awards.

1995 ACS Award in Polymer Chemistry sponsored by Mobil Chemical Company